

## BIOMASS CHAR AND LIGNIN: POTENTIAL APPLICATION

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### INTRODUCTION

It is well known that biomass can be converted to a liquid product (usually called bio-oil or biofuel) using fast pyrolysis. This technology has now reached commercial stage. For example, two commercial plants using this technology (ENSYN Technologies Inc. of Ottawa, ON, Canada) are being operated by Red Arrow Products, Co., Inc. in Wisconsin (~ 50 tonnes/day). Also, a pilot demonstration unit (3 tonnes/day) is being operated in Galicia, Spain, using a bubbling fluidized bed (i.e. using the technology developed at the University of Waterloo, Canada). In these processes, the product slate consists of approximately 70 wt% liquid, 15 wt% char and 15 wt% gas. Thus, a certain amount of char is produced which needs to be disposed of (either by burning or some other method).

Furthermore, laboratory studies on upgrading this bio-oil using a zeolite (such as HZSM-5) have shown that in addition to hydrocarbon content in the liquid product, an additional amount of char (~ 10 – 20 wt%) also is produced. This char is in addition to the coke formed on the catalyst.

Also, lignin is a byproduct of little or no commercial value in the pulp and paper industry. In the dominant pulping process, namely kraft pulping, it is used primarily as a low grade fuel in the recovery boiler. It would be highly desirable to produce value-added products from lignin. Not only that, but its mere removal from the kraft process would allow many pulp mills, which are recovery boiler capacity limited to increase their pulp production.

Furthermore, an alternative pulping process (using an organic solvent vs. the more common kraft process) typically employs an organic solvent (or a solvent-aqueous mixture) with an acid catalyst for delignification at prescribed temperature and time sequences. An "organosolv process", the Alcell® process has been used by Repap Enterprises Corporation Inc. on an industrial demonstration scale in Miramichi, NB, Canada. We have attempted to convert the lignin produced from this process (Alcell® lignin) using acetone as solvent and treating it with HZSM-5 catalyst.

Thus, the thrust of this paper is to attempt to convert these materials – chars and lignins that are essentially waste materials – to useful and value-added products using steam gasification and catalytic upgrading techniques.

### EXPERIMENTAL

#### (a) Steam Gasification of Chars and Lignins

Two chars were gasified with steam. Char A was obtained during the bio-oil production from biomass and was supplied by ENSYN Technologies Inc. of Ottawa, Canada. Char B was obtained during the catalytic upgrading of bio-oil using HZSM-5 catalyst (These runs were carried out in our laboratory).

Both the chars (A and B) were characterized thoroughly. The physical characteristics determined were: density, ash content, elemental analysis (CHN analysis), methylene blue number, Iodine number and BET surface areas (using ASAP Micromeritics 2000 equipment). The results are shown in Table 1.

Lignin (Kraft-1) was obtained from mostly spruce wood at Irving Pulp and Paper Company, New Brunswick, Canada. It was found to have a number average molecular weight of 1750 g/mol<sup>3</sup>.

The lignin used for converting to hydrocarbons (using acetone as the solvent) was the Alcell<sup>(R)</sup> lignin. It was supplied by Alcell Technologies Inc. (Miramichi, New Brunswick, Canada) where it was isolated from a hardwood mixture in a demonstration facility. This lignin, available as a free-flowing powder of 20-40 µm median particle size, is hydrophobic, has a weight-average molar mass of <2000 g/mol, an ash content of <1 wt %, a C and H content of 66 and 6 wt %, respectively. Other typical characteristics of Alcell<sup>(R)</sup> lignin have been presented elsewhere<sup>1,2</sup>.

### (i) Experimental Procedure for Steam Gasification of Chars and Kraft Lignin

Steam gasification was carried out at atmospheric pressure in a continuous down-flow fixed-bed microreactor operated at 600, 700 & 800°C. The reactor was 500 mm long, 11 mm i.d. 1-2 g of lignin/char was held on a plug of quartz wool, which was placed on a supporting mesh inside the microreactor. The top of the lignin/char sample was covered by another quartz wool plug of ~40 mm length. Each steam gasification run required the feeding of steam into the reactor at the prescribed feed rate.

A typical run was carried out as follows: the reactor was filled with a sample of accurately weighed lignin/char (1-2 g) mixed with quartz chips (mass ratio 1:8). The system was tested for leaks prior to the steam gasification run. Heating was started and when the reactor attained a temperature of ~110°C, water was fed into the reactor at the desired flow rate using a micrometering syringe pump (Eldex model A-60-S). The reactor had a long preheating section. Thus, there was sufficient time for the water introduced into the reactor to vaporize and to produce steam (at the gasification temperature used) before contacting the lignin/char. It took approximately 25-30 min to reach the desired operating temperature. The run was continued for another 30 min until no more gas was produced from the reactor. The product leaving the reactor was condensed and separated into liquid (mainly unreacted water) and gaseous fractions. The liquid product fraction was collected in a glass trap, which was cooled with flowing tap water. The gases were collected over saturated brine.

After each run, the spent lignin/char was removed from the reactor and weighed. The difference in combustible content of lignin/char before and after the run was taken as an estimate of the lignin or char converted.

### (ii) Experimental Procedures for Catalytic Conversion of Alcell® Lignin Using HZSM-5 Catalyst

In this study, HZSM-5 zeolite catalyst was used for upgrading lignin (dissolved in acetone). This work was based on our earlier work which showed that biomass-derived oil (liquid product obtained from fast pyrolysis of biomass) and plant oils (such as canola) can be converted to value-added products such as aromatic hydrocarbons and cyclic aliphatic hydrocarbons over HZSM-5 zeolite catalyst.

The experiments were conducted at atmospheric pressure using a continuous down-flow fixed bed micro-reactor operated over a temperature range of 500 – 650 °C and WHSV range of 2.5 – 7.5 h<sup>-1</sup> (for the lignin and acetone solution). The reactor was a 400 mm long, 11.5 mm ID (made of 316 SS) placed coaxially in a furnace. The catalyst particle size range was 500 – 1410 µm. The catalyst was held by a plug of quartz glass wool which was placed on a supporting mesh inside the micro-reactor.

Additional details on the catalyst preparation and characterization are given elsewhere<sup>4</sup>.

The Alcell® lignin was found to be completely soluble in acetone. The liquid feed for the present study was prepared as a solution of this lignin in acetone in the weight ratio of 1 to 2 (lignin to acetone); other experimental details and product analysis details are given elsewhere<sup>4</sup>.

## RESULTS AND DISCUSSION

### (a) Steam Gasification of Chars and Lignin

Steam gasification of chars was carried out at three temperatures (600, 700 and 800 °C) and four steam feed rates (5, 10, 15 and 20 g of steam per h per g of char). It was found that the best char conversions were obtained at a temperature of 800 °C and steam feed rate of 10 g/h per g of char.

Table 2 shows the char and lignin conversion, total gas produced and product gas composition at the optimum conditions of steam feed rate at 10 g/h per g char and a temperature of 800 °C.

The results show that catalytic char (char B) is more reactive, i.e. has a higher conversion than commercial char (char A). Also, its heating value is higher 788 Btu/SCF vs 566 Btu/SCF (for char A). The product gas, has a high concentration of methane for char B (46.2 wt% vs. 41.1 mol %).

On the other hand, char A (commercial char) produces a higher volume of gas (124 L/100 g char) than char B which produced only 97L of gas / 100 g char. Furthermore, the product gas was rich in hydrogen (33.6 mol % for char A vs. 11.6 mol % for char B).

Kraft-1 lignin was the most reactive of all the three materials (94 wt%) and also, resulted in the highest amount of product gas (180 L/100 g lignin). It also produced the highest amount of hydrogen (36.9 mol %) amongst the three materials studied. However, the product gas heating value was the lowest (550 Btu/SCF) of the three.

#### (b) Catalytic Conversion of Alcell® Lignin Over HZSM-Catalyst

As has been stated earlier, Alcell® lignin was solubilized completely in acetone in the weight ratio 2:1 of acetone to lignin. This solution was used as the feed for lignin conversion.

The experimental conditions and mass balance are shown in Table 3. The lignin conversion to gaseous and liquid products greatly depends on the operating conditions and ranged from 50-85 wt%. The maximum conversion was 85 wt% and was obtained at 600 °C and a WHSV of 2.5 h<sup>-1</sup>. Also, with increasing reaction temperature, increasing amounts of gas are produced with decreasing yields of liquid and solid residue (carbonaceous deposits left on the catalyst). The dramatic rise in total gas yield from 500 °C to 650 °C for a WHSV of 5 h<sup>-1</sup> is indicative of the extensive cleavage of the major bonds in lignin (-C-O-C- and -C-C-) via demethoxylation, demethylation, deoxygenation and pyrolytic reactions with increasing temperature. The maximum amount of liquid product (43 wt%) was obtained at 550 °C and a WHSV of 5 h<sup>-1</sup>. It is interesting to note that the yield of liquid produced does not decrease as much as the solid residue (coke and char), which is reduced by almost 50% when the temperature was increased from 550 °C to 600 °C. However, the liquid product decreased dramatically to 11 wt% when the temperature was increased to 650 °C at a WHSV of 5 h<sup>-1</sup> due to more gas formation.

The char was the solid carbonaceous material which formed primarily above the catalyst bed. The formation of this material was exclusively the result of the thermal sensitivity of the lignin used, since cracking of the acetone solvent alone at these conditions only produced a gas. It is well known that char and coke formation is a major problem in any cracking process. Char and coke formation in the cracking of organic materials such as lignin is probably due to the condensation or polymerization reactions dominating over the cracking reactions.

In each experimental run, a mass balance over the entire process was found to be 95% or better.

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**Table 1: Various Characteristics of Chars and Lignins**

Char/ Lignin	Density g/mL	Ash Content wt %	Elemental Analysis				Methylene Blue No. mg/g	Iodine Number mg/g	BET surface area m <sup>2</sup> /g
			C	H	O	N			
Char A	0.20	4.2	79.6	2.4	18	0	1.5	4.7	0.25
Char B	0.10	0.25	75.5	4.8	19.7	0	10	45	51
Kraft 1 Lignin	0.35	4.1	66.08	4.9	34.3	0	0.5	1.1	0.75

**Table 2: Products Obtained and Conversions for the Steam Gasification of Chars and Lignin**

Basis: 100 g of char or lignin

	Char B	Char A	Kraft -1 Lignin
Conversion, wt%	84.2	65.2	94.0
Total gas produced, L	97	124	180
Total gas produced, SCF	3.43	4.38	6.36
Gas Heating Value, Btu/SCF	788	566	550
<b>Gas Composition, mol%</b>			
<b>Component</b>			
H <sub>2</sub>	11.6	33.6	36.9
CO	14.4	11.4	17.1
CO <sub>2</sub>	14.9	13.4	9.5
CH <sub>4</sub>	46.2	41.1	35.5
C <sub>2</sub>	8.0	0.3	0.9
C <sub>3</sub>	3.4	0.2	0.1
C <sub>4</sub> <sup>+</sup>	1.5	0	0
Total	100.0	100.0	100.0

**Table 3: Overall Material Balances and Liquid Product Composition from the Conversion of Alcell® Lignin Over HZSM-5**

Temp., °C	500	550	600			650
WHSV, h <sup>-1</sup>	5	5	2.5	5	7.5	5
<b>Yield of Products*, wt%</b>						
Gas	11	19	51	54	58	68
Liquid	39	43	34	30	22	11
Char+Coke	50	33	15	16	20	21
Conversion	50	67	85	84	80	79
<b>Composition, wt% of Liquid Product</b>						
Alcohols	-	-	-	-	0.3	-
Ketones	-	-	-	-	0.2	-
Benzene	8.6	9.4	9.3	13.6	14.5	14.4
Toluene	33.1	36.7	31.0	42.4	41.9	43.7
Xylenes	31.5	33.0	25.0	22.7	24.8	21.0
Ethyl Benzene	3.0	2.1	2.2	1.9	1.5	1.3
Propyl Benzene	4.2	2.5	3.7	1.3	1.5	1.0
C <sub>9</sub> <sup>+</sup> Aromatics	9.0	5.1	6.4	6.0	3.1	3.0
Total Aromatics	89.4	88.8	74.6	87.9	87.8	84.4
Total Aliphatic Hydrocarbon	-	-	-	0.5	0.6	0.5
Unidentified	10.6	11.2	25.4	11.3	11.3	15.1
Total	100	100	100	100	100	100

\*wt% of lignin in the feed

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